Plutonium Association with Selected Solid Phases in Soils of Rocky Flats, Colorado, Using Sequential Extraction Technique

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ABSTRACT

Plutonium contamination in the soil environs of Rocky Flats, CO, has been a potential health risk to the public since the late 1960s. Although the measurement of total activity of Pu-239 + 240 in the soil is important information in appraising this risk, total activity does not provide the information required to characterize the geochemical behavior that affects the transport of Pu from the soil and vadose zone to groundwater. A sequential extraction experiment was conducted to assess the geochemical association of Pu with selected mineralogical and chemical phases of the soil. In the surface horizons, Pu-239 + 240 was primarily associated with the organic C (45-65%), sesquioxides (20-40%), and the residual fraction (10-15%). A small portion of Pu-239 + 240 was associated with soluble (0.09-0.22%), exchangeable (0.04-0.08%), and carbonates (0.57-7.0%) phases. These results suggest that under the observed pH and oxic conditions, relatively little Pu-239 + 240 is available for geochemically induced transport processes. Uncommon hydrogeochemical conditions were observed during the spring of 1995, which may have facilitated a partial dissolution of sesquioxides followed by desorption of Pu resulting in increased Pu mobility. Systematic errors in the sequential extraction experiment due to postextraction readsorption were evaluated using Np-237 tracer as a surrogate to Pu-239. The results suggested that postextraction readsorption rates were insignificant during the first 30 min after extraction for most chemical and mineralogical phases under study.

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Abbreviations: CEC, cation exchange capacity; CBD, citrate-bicarbonate-dithionite; ORNL, Oak Ridge National Laboratory.

T HE ROCKY FLATS PLANT located approximately 20 km northwest of Denver, processed Pu-239 + 240 for nuclear weapons from 1952 until 1989, when production was suspended. Plutonium contamination at Rocky Flats Plant resulted from Pu-contaminated cutting oil that leaked into the soil from drums stored at an outdoor storage site locally known as the 903 Pad (Krey and Hardy, 1970; Seed et al., 1971). Plutonium particles entrapped in the fine fraction of the surface soils were subsequently lifted by winds and deposited on soils in an east and southeast-trending plume (Krey and Hardy, 1970; Seed et al., 1971; Litaor, 1995; Litaor et al., 1995).

The spatial and vertical distributions of Pu around the site have been characterized by several investigators. Little and Whicker (1978) reported that Pu-239 activity in soils east of the former storage site increased with decreasing particle size. Soil profiles sampled in 3-cm increments to a 21-cm depth indicated a strong correlation between Pu activity and the submicron size particles. Krey et al. (1976) reported that 90% of the total Pu activity resides in the upper 10 cm of the soil profile.

More recently, Webb et al. (1993) and Litaor et al. (1994) found that most of the Pu activity is still confined to the surface horizons (0-12 cm) regardless of soil type, distance, or direction from the contamination source. These findings strongly suggest that Pu mobility in soils east of Rocky Flats is limited. However, occasional elevated activities of Pu-239 + 240 (~ 2 mBq L^{-1}) were found in filtered seep water located 400 m east of the former storage site. It has been suggested that some of the Pu may be transported by runoff (Webb et al., 1993), and macropore flow (Litaor et al., 1994; Litaor et al., 1996). Prediction of Pu transport in the soil and vadose zone will be significantly improved if the Pu distribution and association with the various solid phases of the soil are well defined.

Conceptually, the soil can be partitioned into specific fractions that can be extracted selectively by using appropriate extractants (Tessier et al., 1979). Sequential dissolution techniques which *selectively* extract soil material with resulting release of its associate trace elements have been extensively used in soil studies and geochemical exploration (Beckett, 1989). The partitioning of a given metal obtained by sequential extraction is operationally defined, as it is influenced by experimental factors such as the choice of reagents, the time of extraction, and the ratio of extractant to soil (Tessier et al., 1979). However, inherent analytical problems such as incomplete selectivity and postextraction readsorption may seriously affect the extracted metal concentrations (Rendell et al., 1980; Gruebel et al., 1988; Kheboian and Bauer, 1987; Belzile et al., 1989).

The objectives of the present study are: (i) to determine Pu association in the soluble, exchangeable, carbonate, organic C, sesquioxide, and the residual fractions of contaminated soils using a selective sequential extraction procedure; and (ii) to assess the effect of the postextraction readsorption during the sequential extraction procedure.

METHODS

Field Sampling

Five soil pits along a contaminated toposequence were excavated with a backhoe and sampled for actinide analysis, and for physical, chemical, and mineralogical properties (see Litaor et al., 1994 for details). The number of pits investigated and their exact positions along the toposequence was determined by a ground penetrating radar survey that was used to locate subsurface lateral discontinuities (Litaor et al., 1994, 1996). The five pits were approximately 250 m east of the former storage site (Fig. 1) and 6 to 1 m above groundwater. Each pit was approximately 5 m long, 1 m wide, and 1 m deep. Each soil sample was collected from within a horizontal cavity dug into the pit face at the selected horizon. A bottom-to-top sampling sequence was adopted to reduce the risk of cross contamination. Sampling for the present work was conducted

by genetic horizons at each pit. Additional sampling using fixed incremental depths was performed concurrently and described by Litaor et al. (1994).

Sequential Extraction Experiment

The soil preparation procedures consisted of drying, grinding, and sieving through an 88-μm sieve. This sieving fraction was chosen to aid complete dissolution of organic C, sesquioxides, and the soil residue. Partitioning of the specific soil fractions was conducted on 3- to 10-g subsamples (depending on the expected Pu activity) using selective extractants in a slight modification of the procedure described by Tessier et al. (1979). Briefly, the soluble Pu was obtained by shaking the soil with distilled water for 24 h using a mechanical shaker. Next, the exchangeable Pu fraction was extracted with a 0.01 M calcium chloride solution, followed by extraction of carbonate with a 0.5 M sodium acetate–acetic acid buffer solution, adjusted to pH 5 as recommended by Nelson (1982). Organic C was then removed by three successive extractions with sodium hypochlorite at pH 9.5 (Hoffman and Fletcher, 1981). This treatment was found to be 98% efficient in removing the oxidizable organic C fraction (Lavkulich and Wiens, 1970). Sesquioxides were dissolved using the citrate–bicarbonate–dithionite (CBD) method (Jackson et al., 1986), which is superior to other methods since it dissolves amorphous sesquioxides more completely. Effective phase separation after each extraction was accomplished by ultracentrifugation at 25 000 rpm for 30 min. After each sequential extraction step, the soil was washed with deionized water to remove the residual reagents from the previous extraction. The volume of the rinse water was kept to a minimum (10–30 mL) to avoid excessive solubilization of the organic matter. Initially, wash solutions from each extraction were analyzed for Pu activity. The Pu activity in these washes was below the detection limit, so these washes were discarded in subsequent samples. After removal of the above fractions from the soil, the residue (primary and clay minerals) was completely dissolved using pyrosulfate fusion in platinum crucibles as described by Sill (1976).

Plutonium-242 was added to the leachates from the sequential extraction as a tracer to track the Pu-239+240 recovery through the following separation process. Plutonium in each sample was first concentrated using the calcium oxalate coprecipitation technique described by Yamato (1982). The calcium oxalate was then filtered, dried, and ashed at 550°C overnight. The filters were wet ashed with concentrated HNO_3 and the residue dissolved in 8 M HNO_3. Plutonium extraction was performed using the ion exchange methods described by Talvitie (1971). The eluent fraction containing Pu was evaporated to dryness and prepared for alpha spectroscopy by microprecipitation on NdF (Hindman, 1983; Sill and Williams, 1981). The samples were counted on 450 mm^2 silicon surface barrier detectors. Approximately 15% of the sample load was reagent blanks and replicate analysis for quality control. The coefficient of variation for all propagated uncertainties of the entire analytical process was better than 30% and about 5% for the high activity level samples.

Because Pu-239 and Pu-240 could not be resolved by alpha spectroscopy, all values are reported as Pu-239+240. The lower limit of detection for Pu-239+240 as calculated from the equation of Seymour et al. (1992) was 2.8 ± 1.2 mBq.

Postextraction Readsorption Experiment

The magnitude of postextraction readsorption was tested using Np-237 as a tracer. Originally, we intended to use Pu-237 because it is easy to measure (gamma emitter), and expected to behave identically to Pu-239 in soils. However, the end of the cold war eliminated the global production of Pu-237; thus, Np-237 was selected as a surrogate for Pu-239 because its environmental chemistry is quite similar to Pu (Allard et al., 1980). Spikes of Np-237 (1.66 Bq/g $\cong$ 100 dpm g^{-1}) were added to each of the supernatant-solid fractions from two soil samples in duplicates after each extraction step. The postextraction readsorption was evaluated as a percentage of the spike recovered from the soil fractions over time. The Np-237 tracer was measured by gamma spectroscopy using a shielded thin NaI(TL) crystal (Bicron Corp., Newbury, OH), connected to a multichannel analyzer.

Because of the length and cost of the postextraction readsorption experiment, only two samples were thoroughly analyzed. The two selected samples (AB and 2BCg of Pit 1) represent typical geochemical conditions in the study site (Table 1) except for the organic C content. The A horizon was excluded from the postextraction readsorption experiment to minimize the energy interference between Np-237 (30 and 86 keV) and Am-241 (60 keV), a radionuclide present in the A horizon (Litaor et al., 1994).

Soil Properties

Cation exchange capacity (CEC) was determined by saturation with 0.4 M Na acetate–0.1 M NaCl, followed by washing with 60% ethanol, and replacing the index cation by 0.5 M Mg(NO$_3$)$_2$ (Rhoades, 1982). Organic C content was determined by dichromate oxidation and titration with FeSO$_4$ (Nelson and Sommers, 1982). The CaCO$_3$ content was determined by a modified pressure calcimeter method described by Nelson (1982). Sesquioxides (Fe, Al, Mn) were extracted using the citrate–bicarbonate–dithionite method (Jackson et al., 1986) and determined by inductively coupled plasma emission spectrometry. Minerals in the clay fractions were identified by standard x-ray diffraction techniques. Semiquantitative estimates of mineral abundance were made in measuring peak intensities and by comparison with diffractograms of reference clay minerals (Moore and Renolds, 1989). Thin-sections were made for each genetic horizon and the primary minerals were identified using a petrographic microscope.

RESULTS AND DISCUSSION

General Characteristics

Most of the soils under study were characterized by relatively large amounts of organic C and sesquioxide, and moderate CEC (Table 1). Pit 1 located at the toeslope position (Fig. 1), was classified as a fine-loamy, mixed (calcareous), mesic Cumulic Haplustoll, and exhibited the least amount of pedogenesis with depth. Pits 2 to 4, located along a colluvial footslope position, were classified as a fine-loamy, mixed, mesic Aridic Argiustoll, whereas Pit 5, located at a steep backslope position was classified as a loamy-skeletal, mixed mesic Aridic Argiustoll. Pits 2 to 5 exhibited argillic horizons, with a considerable increase of sesquioxides especially in Pits 3 to 5 (Table 1) and clay content (not shown) with depth. The pH of the soils varied between 6.5 to 8.0 with a mean of 7.3 ± 0.5. In general, the pH of the soils increased with depth followed by increased of CaCO$_3$ content in some of the soil samples.

Plutonium-239+240 activity in the top soil horizons ranged from 3920 to 18 200 Bq kg^{-1}, with mean activity of 8480 Bq kg^{-1}. The distribution of Pu-239+240 activity

in the samples collected from the five pits showed that >90% of the Pu isotopes is residing in the upper 18 cm of the soil (Table 2). The activity of Pu-239+240 at all locations decreased with depth to near background levels (i.e., global fallout ~ 1.5 Bq kg^{-1}) in the deepest horizons (>1 m). The observed decrease in Pu-239+240 activity with depth was consistent with findings of previous studies (Little and Whicker, 1978; Webb et al., 1993; Litaor et al., 1994).

Sequential Extraction Experiment

Mass balance calculations showed that the Pu activity derived from the sequential extraction experiments (Table 3) agreed well with the total Pu determinations (Table 2). These results indicate that little Pu has been lost during the extensive washing and extracting of the various chemical and mineralogical phases of the soils. Because 90% of the Pu-239+240 was observed in the A horizons, most of the geochemical analysis of the results from the sequential extraction experiment was limited to the surface horizons. Furthermore, the extreme low activity of Pu-239+240 in the subsurface horizons made the interpretation of the sequential extraction results from the subsurface horizons difficult.

Extremely small amounts of soluble and exchangeable Pu (<1%) were observed at all depths and sampling locations (Table 3). The findings that soluble and exchangeable Pu are negligible suggest that most of the Pu is not readily available for leaching through the soil. Furthermore, the insignificant amount of readily available Pu supports an earlier vegetation study (Arthur and Alldredge, 1982), which showed minimal Pu uptake by physiological processes at Rocky Flats, CO. Similar results for soluble and exchangeable Pu were reported in UK soils contaminated by effluent discharge from a nuclear installation (Cook et al., 1984), in Spanish soils contaminated by ignition of Pu from four nuclear bombs following an air accident over Palomares (Iranzo et al., 1991), and in Ukrainian soils contaminated by the Chernobyl accident (Goryachenkova et al., 1991).

Plutonium associated or bound with carbonates in the A horizons ranged from 1 to 7% (Table 3). There was no clear relationship between the CaCO₃ content of the soil (Table 1), the total Pu in the soil (Table 2), and the Pu associated with carbonates (Table 3). Insufficient specificity of the 0.5 M sodium acetate–acetic acid solution in the dissolution of carbonates is probably the main reason for this lack of correlation. The lack of specificity of the NaOAc–HOAc reagent for carbonates was reported elsewhere. For example, Tessier et al. (1982) showed that, in sediments characterized with low carbonates, 1 M NaOAc–HOAc solution desorbed Pb, Cu, and Zn from the surfaces of iron oxyhydroxides. They argued that desorption of surface-bound metals was the dominant mechanism during the carbonate metals extraction, rather than dissolution of iron oxyhydroxides, which would release occluded metals. Similarly, Jouanneau et al. (1983) showed that 36% of Mn-oxyhydroxide coatings were removed during carbonate dissolution using 1 M

NaOAc–HOAc following the procedure outlined by Tessier et al. (1979).

Plutonium associated with organic C in the surface horizons varied between 2520 and 9160 Bq kg^{-1}. Organic C exhibited the highest affinity for Pu (up to 65% in the A horizons) in all depths and sampling locations (Table 3). A good correlation was found between Pu activity and organic C content ($r = 0.72$, $P < 0.01$). Under the pH and redox potential of the soil, most of the Pu is insoluble (Martell, 1975; Rai et al., 1980), and the dominant solid phases of Pu in the soils of Rocky Flats are probably Pu oxides. Thus, the interaction between the solid organic matter and the solid phase of Pu in the soil probably can be described as a *physical adsorption*. This somewhat poorly defined term was also used by Triay et al. (1991) and described a retardation mechanism between Pu and solid mineral phases. However, the exact nature of this association is poorly understood.

Bondietti et al. (1976) found a similar strong affinity between Pu and organic C (up to 82%) in soil from Oak Ridge National Laboratory (ORNL) in Tennessee. They speculated that some of the Pu–C bonding derived from low molecular weight organo–Pu complexes sorbed onto solid phase organic matter. Cook et al. (1984), Livens et al. (1986), and Bunzl et al. (1995) found that most of the Pu is associated with organic matter (50–70%), but did not identify a binding mechanism. Livens et al. (1987) revisited the issue of sorption mechanism of Pu in a soil from the UK and suggested that 65% of the Pu was associated with humic acids through the formation of poorly defined iron–organo–plutonium complexes. Somewhat similar results were found in Ukrainian soils affected by the Chernobyl accident (Goryachenkova et al., 1991). They reported that up to 54% of the Pu in a *leached chernozem* was associated with complexes of humic acids and Fe, and Al oxyhydroxides, although this fraction varied significantly among different soil types. They also reported that Pu was associated with humin (up to 15.3%) and soluble organic compounds (up to 42%) that varied greatly among soil types.

A desorption study conducted on Pu contaminated soil located in ORNL (Bondietti et al., 1976) showed that even 30 yr after contamination, only a small amount of Pu was desorbed under experimental conditions favoring complete removal. As was mentioned above, up to 82% of the Pu in this soil was associated with organic C. Hence, the present finding that a large percentage of Pu is associated with organic C suggests that under the *normal* oxic conditions observed in the soils of Rocky Flats (see below), Pu is largely immobile.

A significant amount of Pu (19–42%) was associated with sesquioxides (Table 3). This value is probably inflated somewhat (~10%) due to the postextraction readsorption phenomenon (see below). A high correlation ($r = 0.88$, $P < 0.001$) was observed between sesquioxide content (Table 1) and CBD extracted Pu activity (Table 3) in the A horizons across the study site. The highest CBD-extractable Pu activity was observed in Pit 5, which also exhibited the highest sesquioxides content.

The Pu associated with sesquioxides was probably occluded due to periodical dissolution and reprecipitation

cycles of iron oxyhydroxides. Soil color (Munsell Soil Color Charts) of the subsurface horizons varied from 7.5YR6/8 (highly oxidized) to 2.5Y5/0 (highly reduced), which suggests that dissolution and reprecipitation cycles occur in these soils. The spring and early summer of 1995 were unseasonably wet. The depth of precipitation at the site during the months of April and May exceeded 24.94 cm, which is >200% the average precipitation for this period (E.M. Zika, 1996, personal communication). Probability analysis of the precipitation depth suggested that the recurrence interval for the frequency and duration of the observed rain in April and May of 1995, is approximately 25 to 50 yr. Starting on 17 May 1995, the soil became completely saturated for at least 65 d (Fig. 2), where significant water flux (-2 to 10 m^3 m^{-2} d^{-1}) was measured in the soil (M.I. Litaor et al., unpublished data). This water flux most likely originated from a well developed network of west- to east-trending paleostream drainages incised into the pediment surface beneath the Rocky Flats alluvium (USDOE, 1995b, Fig. 3.5-6 to 3.5-16). A long section of the buried paleostream is located below the former storage site (Fig. 1) and upslope from the study site. The water-filled paleostream generated laterally flowing water across the study site, which transformed the generally oxic soils to water logged soils. Field observations and real time in-situ measurements of piezometric surface (Fig. 2) (see Litaor et al., 1996 for details of the monitoring system), clearly indicated that the water reached the surface of the study site. Soil moisture content persisted at 40% (Fig. 2), which resulted in highly reducing conditions (M.I. Litaor, 1995, unpublished data), which in turn may have initiated a partial dissolution of Fe-oxyhydroxides followed by desorption of Pu to soil solution. If groundwater recedes quickly, the partially dissolved Fe-oxyhydroxides will reprecipitate and subsequently occlude Pu. However, if the groundwater level stays high for an extended period of time as demonstrated in Fig. 2, Pu released from the dissolution of Fe-oxyhydroxides may be transported to larger distances than previously observed (Litaor et al., 1996). Moreover, under these anoxic conditions, certain bacteria may even dissolve the insoluble Pu-oxides (Rusin et al., 1994), and may further enhance its mobility and bioavailability. This hydrogeochemically induced transport mechanism was not envisioned under any environmental condition or hydrogeochemical modeling scenarios (USDOE, 1991). Evidence for similar hydrogeochemical remobilization of actinides was recently reported by Hursthouse and Livens (1993), who observed enhanced actinide activity (i.e., Pu, Am, and Np), and remobilization in highly anoxic soils located along an estuary near Sellafield, UK. The potential increased mobility of Pu under these hydrogeochemical conditions should be considered in assessing the remedial alternatives of a site, where the stated remediation goals are reduction of toxicity, mobility, and volume of radionuclides through treatment (USDOE, 1995a).

A literature survey of Pu activity associated with sesquioxides showed large variability, probably due to inconsistency in the application of the sequential extraction procedure and the highly variable nature of the different soils. For example, Iranzo et al. (1991) reported that only 0.9 to 2.4% of the Pu was associated with sesquioxides. This surprisingly small percentage may have resulted from the use of 0.1 M Na-pyrophosphate to dissolve organic C and 0.175 M ammonium oxalate to dissolve sesquioxides. Both reagents are significantly weaker than those used in the present study, potentially resulting in incomplete dissolution of organic C and sesquioxides and consequently underestimating the fraction of Pu associated with these solid phases. Livens et al. (1986) found that 15 to 35% of the Pu was occluded with amorphous Fe- and Mn-oxyhydroxides. These results are in good agreement with the present study although they also used 0.1 M Na-pyrophosphate to dissolve organic C and 0.175 M ammonium oxalate to dissolve sesquioxides. They acknowledged that the 0.1 M Na-pyrophosphate may remove <30% of the organic C, but suggested that this reagent is suitable for soils with a high ash content. Goryachenkova et al. (1991) reported 43 to 66% of the Pu was associated with sesquioxides, which is significantly higher than the current work. However, they did not provide a detailed account of the experimental sequence and conditions in which Pu associated with organic C was extracted. Muller (1978) reported 73 to 88% of the Pu was associated with sesquioxides, probably because only 2 to 13% was associated with organic C. The reason for the lower association with organic C may have resulted from the different extractant used (0.5 M NaOH), the extreme low initial loading of Pu on these Ohio soils, and low organic C content.

Plutonium associated with the residual component of the soil varied between 10 to 15% in the A horizons (Table 3). The residual fraction represents Pu associated with the primary and clay minerals (Table 4), as well as insoluble discrete particles of plutonium oxides (see below). A literature survey regarding the magnitude of Pu associated with the residual fraction also showed extreme variations. For example, Cook et al. (1984), Muller (1978), and Livens et al. (1986) reported similar results of Pu associated with residual phase (8.1, 2–19, and 7–18%, respectively) to the present study. On the other hand, Goryachenkova et al. (1991) reported only 0.5 to 1.6% of Pu associated with the mineral fraction, whereas Iranzo et al. (1991) reported that 91.1% of the total Pu was associated with the residual phase. The above variations may be explained by differences in the presumed selectivity of the sequential extraction procedures, soil types, and the form of Pu released to the environment as was demonstrated by Goryachenkova et al. (1991).

The adsorption mechanism of the Pu associated with the residual fraction is also poorly understood. Livens et al. (1986) speculated that the residual fraction represents Pu bound to the lattices of clay minerals or irreversibly sorbed onto humin, whereas Iranzo et al. (1991) speculated that the Pu was incorporated in the crystalline structure of weathering resistant minerals such as chlorite, biotite, complex oxides of Ti, Fe, and Mn, and coprecipitated with dolomite, ankerite, and phosphate.

minerals. No supporting evidence for either speculation was provided. Moreover, specific adsorption or incorporation of Pu into the lattices of the clay and primary minerals observed in Rocky Flats soils is difficult.

Perhaps the relatively high percentage of Pu associated with the residual fraction can be explained by the presence of discrete Pu particles in soils. The term *discrete particle* is defined here as an agglomerated particle containing a large number of host soil grains and Pu oxides. McDowell and Whicker (1978) studied soil collected from a site approximately 100 m west of Pit 1 and isolated a large PuO_2 particle of 6.86 μm diameter. Additional work showed that the particle was an agglomerate of smaller, probably submicron particles. Fowler et al. (1968) studied soils collected from Palomares, Spain, the same site studied by Iranzo et al. (1991) and found Pu in the form of discrete particles, probably weakly aggregated to soil particles. Hence, the fraction of Pu associated with the residual phase probably originated from Pu oxide particles that resisted dissolution by all the reagents applied during the sequential extraction experiments preceding the residual fraction determination.

Postextraction Readsorption

The postextraction readsorption results suggested that moderate amounts of the Np-237 tracer were immediately lost from the supernatant following the soluble and exchangeable extractions (Table 5), and these losses increased significantly with time. The main reasons for these losses are probably the low ionic strength of the extractants, their neutral pH, and the lack of a strong counter ion in the extractant. These results do not necessarily invalidate the sequential extraction experiment, because in general, Pu is not soluble in the soil environment (Martell, 1975; Rai et al., 1980), nor can it successfully compete with the major cations (e.g., Ca, Mg) for cation exchange sites.

There were no significant losses of the Np-237 tracer following the removal of $CaCO_3$ and sesquioxides (Table 5). The acetate and the citrate–bicarbonate–dithionite are strong complexing ions, which successfully prevented postextraction readsorption. On the other hand, almost 10% of the Np-237 tracer was immediately lost from the supernatant following the destruction of organic C. The postextraction readsorption rates increased significantly with time (Table 5). The readsorbed fraction should be taken into account when the magnitude of Pu associated with sesquioxides is evaluated. There was no significant difference in postextraction readsorption between the AB and the 2BCg horizons, although the AB horizon exhibited 14 times more organic C content (see Table 1). Hence, the results of the postextraction readsorption may be applied to the A horizon where most of the organic C and Pu were found. The above results suggest that the postextraction readsorption did not severely alter the intended fractions of the *selective* sequential extraction protocol as outlined by Tessier et al. (1979). The sequential extraction experiments provided a reasonable fractionation scheme in determining the amount of Pu-239+240 associated with the selected

chemical and mineralogical phases of the soils.

CONCLUSIONS

The physiochemical relationships of Pu-239+240 in contaminated soils of Rocky Flats suggest that most of the Pu is associated with organic C and sesquioxides. The findings support the notion that Pu-239+240 in the soils of Rocky Flats is not readily mobilized under the common pH and redox conditions encountered in these soils. However, unusual hydrogeochemical conditions were observed during the spring of 1995, which may have facilitated a partial dissolution of Fe-oxyhydroxides followed by desorption of Pu, which in turn may have increased Pu mobility. Postextraction readsorption did not significantly affect the results obtained from the sequential extraction experiment.
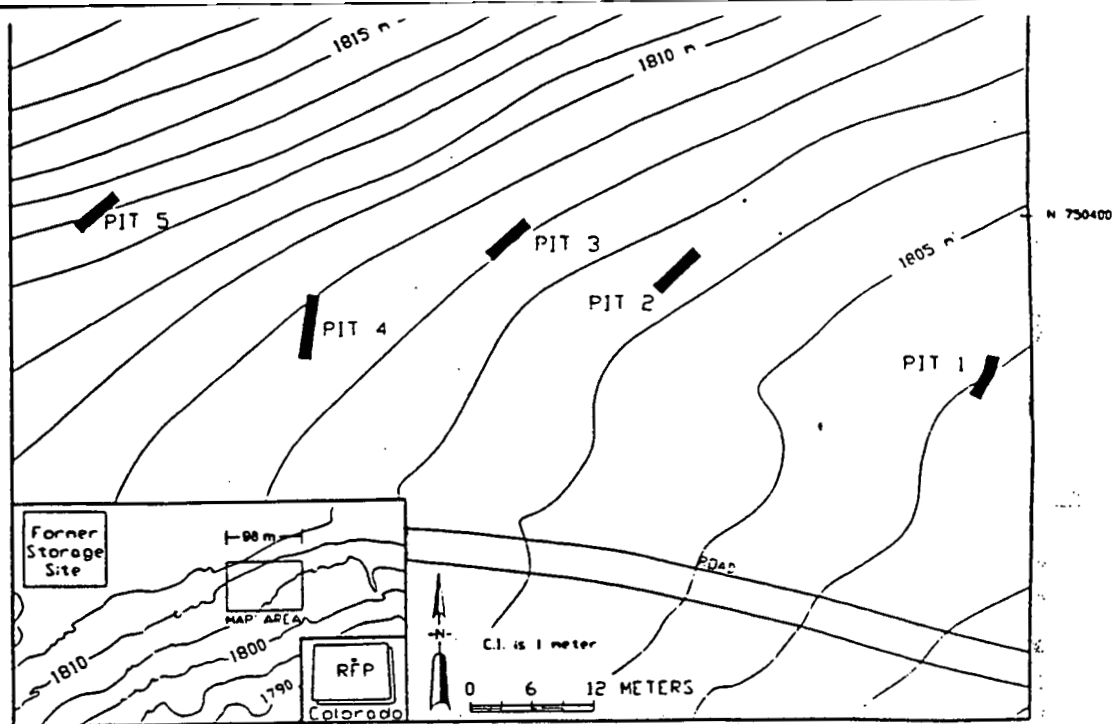
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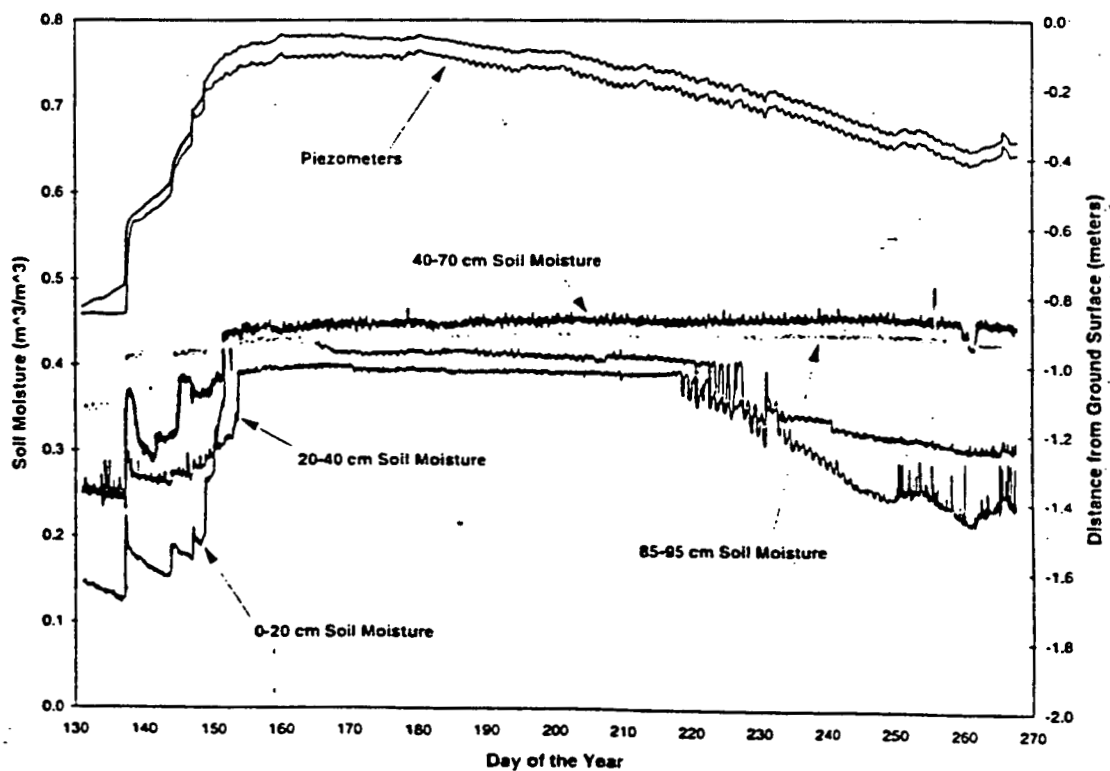
Table 5. Percentage recovery of Np-237 tracer after each sequential extraction as a function of time.

Fraction extractant horizon	Soluble H$_2$O		Exchangeable CaCl$_2$		CaCO$_3$ Na-Acetate		Organic C NaOCl		Sesquioxides CBD	
	AB	2BCg	AB	2BCg	AB	2BCg	AB	2BCg	AB	2BCg
Time (min)										
30	75.9	90.0	73.5	77.4	99.3	100	90.0	90.9	98.1	99.3
	(4.4)†	(0.3)	(0.7)	(7.0)	(0.9)	(0)	(3.4)	(3.8)	(1.1)	(0.06)
100	70.4	82.0	68.4	59.6	97.1	98.6	88.7	89.2	97.4	98.2
	(6.5)	(3.0)	(0.7)	(10)	(1.4)	(0.6)	(0.7)	(2.5)	(0.8)	(0.4)
200	66.9	74.7	63.7	48.3	95.3	95.5	87.1	87.1	95.9	95.9
	(7.5)	(1.4)	(1.6)	(6.8)	(0.4)	(1.4)	(0.2)	(5.8)	(0.06)	(1.2)
500	63.8	66.5	59.6	40.8	92.6	92.1	83.5	84.3	96.3	95.7
	(8.9)	(3.0)	(4.9)	(2.1)	(0.9)	(3.8)	(0.6)	(1.8)	(0.01)	(1.3)
1300	58.4	56.7	49.2	42.7	86.5	90.7	76.9	82.6	94.7	96.6
	(9.2)	(9.1)	(11)	(2.0)	(3.2)	(1.4)	(2.8)	(0.8)	(0.5)	(0.4)
2700	54.4	52.3	46.6	42.0	82.7	86.8	72.9	78.9	93.8	95.4
	(7.2)	(14)	(11)	(0.1)	(1.6)	(0.08)	(1.4)	(2.5)	(1.3)	(2.2)

† The values in parentheses represent standard deviation.

Table 3. Pu-239 + 240 association with selected chemical and mineralogical phases.

Horizon	Depth	Soluble		CEC		CaCO₃		Organic C		Sesquioxides		Residue		Total Pu
	cm	Bq/kg	%	Bq/kg	%	Bq/kg	%	Bq/kg	%	Bq/kg	%	Bq/kg	%	Bq/kg
Pit 1														
A	16	4.8	0.1	1.7	0.04	170	4.3	2520	64.6	780	20.0	420	10.8	3 896
AB	11	0.3	0.2	0.3	0.2	7.5	5.2	92.0	63.8	28.8	19.9	15.1	10.5	144
Bk1	31	0.3	1.8	1.3	7.4	2.0	11.1	9.6	53.7	1.3	7.4	3.3	18.5	17.8
Bk2	18	0.05	0.8	0.3	5.8	0.8	14.6	0.8	14.5	2.8	49.5	0.8	14.5	5.5
Bg	27	0.03	0.8	0.05	1.3	0.3	8.5	1.3	34.0	1.0	25.5	1.1	29.7	3.8
2BCg	20	0.03	0.6	0.02	0.3	0.2	3.3	2.3	46.2	1.3	26.4	1.1	23.1	4.9
Pit 2														
A	7	13.0	0.2	1.7	0.03	410	7.0	3510	59.5	1330	22.4	640	10.7	5 904
Bw	12	5.7	0.1	0.33	0.01	170	4.3	2720	66.3	790	19.1	410	10.0	4 096
Bt	31	0.02	0.02	0.03	0.04	4.5	5.9	56.5	73.9	7.3	9.6	8.0	10.4	76.3
2Bt	55	1.3	12.3	1.00	9.2	2.8	26.1	1.5	13.8	2.3	21.5	1.3	16.9	10.2
3BCgk1	20	0.1	9.4	0.02	1.3	0.1	8.1	0.3	27.0	0.3	27.0	0.3	27.0	1.1
Pit 3														
A	18	8.3	0.1	1.2	0.02	260	3.3	3500	45.2	3230	41.6	750	9.6	7 750
AB	17	0.8	0.4	1.5	0.7	6.5	3.2	130	67.0	37.7	18.8	19.3	9.6	195
Bw	16	0.1	1.7	0.02	0.2	0.3	4.2	5.8	73.0	1.2	14.6	0.5	6.2	7.9
BCg	69	0.1	0.6	0.1	0.7	0.3	1.8	13.7	77.4	3.2	17.9	0.2	1.4	17.6
BCk1	20	0.07	3.6	0.05	2.7	0.05	2.7	0.6	34.2	0.2	11.7	0.8	45.0	1.7
Pit 4														
A	18	6.2	0.1	5.0	0.08	220	3.3	4100	61.8	1290	19.4	1010	15.2	6 631
Bt1	23	0.05	0.1	0.03	0.08	2.5	6.1	29.0	72.5	5.3	13.0	3.3	8.1	40.2
Bt2	36	0.2	0.8	0.10	0.5	1.3	6.3	16.0	76.4	1.0	4.7	2.3	11.1	20.9
BCg	31	0.1	4.5	0.08	3.7	0.1	5.2	1.3	60.1	0.1	6.7	0.4	19.5	2.2
2BCg	20	0.03	0.5	0.03	0.5	0.7	10.4	3.8	59.9	0.3	5.2	1.5	23.4	6.4
Pit 5														
A	15	9.0	0.05	11.2	0.06	100	0.6	9160	50.2	6520	35.7	2430	13.3	18 230
Bt	33	1.5	0.1	0.08	0.01	91.0	6.2	660	45.1	410	27.7	300	20.7	1 462
Btg	72	0.2	3.1	0.03	0.6	1	18.6	3.3	62.1	0.3	6.2	0.5	9.3	5.3

Table 4. Relative abundance (%) of primary and clay minerals in the A horizons of Pits 1 to 5.

Soil horizon Pits 1-5	Depth cm	Primary minerals			Clay minerals		
		quartz	microcline	plagioclase	Smectite	Mica	Kaolinite
A	0–18	30–60	5–30	5–30	5–30	5–60	5–30

Ed: Pits 1–5 below Rule?
cm below Rule?

del Soil, Pits, and 1-5.

9

Table 1. Selected Chemical Properties of the five Soils Under Study

Horizon	Depth	pH	Organic C	CaCO₃	CEC	Fe	Mn	Al
	cm		g kg⁻¹	g kg⁻¹	cmol kg⁻¹		ug/g	

Sesquioxides: Fe, Mn, Al

Horizon	Depth (cm)	pH	Organic C (g kg⁻¹)	CaCO₃ (g kg⁻¹)	CEC (cmol kg⁻¹)	Fe (ug/g)	Mn (ug/g)	Al (ug/g)
Pit 1								
A	0–16	7.4	41	20	28.6	2 030	30	600
AB	16–27	7.7	28	56	30.3	3 280	28	965
Bk1	27–58	8.0	13	122	29.9	2 150	10	740
Bk2	58–76	7.9	16	107	25.8	2 110	4	560
Bg	76–103	7.9	4	90	22.5	1 820	8	530
2BCg	103 +	8.0	2	56	24.4	1 500	7	470
Pit 2								
A	0–7	7.2	100	4	27.4	4 410	140	435
Bw	7–19	7.0	54	3	19.8	4 120	90	450
Bt	19–50	7.0	13	2	22.8	1 060	150	1370
2Bt	50–105	7.0	6	5	19.8	2 950	1340	1580
3BCgk1	105 +	7.5	2	27	26.5	2 200	110	290
Pit 3								
A	0–18	7.0	100	10	27.9	4 080	160	480
AB	18–35	7.1	20	4	23.3	6 380	84	1050
Bw	35–51	7.0	39	2	20.8	7 750	130	1000
BC	51–120	7.7	3	23	29.6	9 660	48	790
BCk1	120 +	7.8	2	35	26.0	2 850	180	265
Pit 4								
A	0–18	6.7	160	6	24.1	4 060	245	480
Bt1	18–41	6.5	18	4	27.9	6 990	240	1110
Bt2	41–77	7.5	6	1	19.7	6 160	93	830
BCg	77–108	6.9	9	9	26.4	11 400	270	980
2BCg	108 +	7.8	4	4	26.4	3 240	9	465
Pit 5								
A	0–15	7.6	69	9	20.5	6 870	230	1180
Bt	15–48	7.6	44	9	21.6	6 790	220	1190
Btg	48–120	6.0	7	9	25.9	15 079	295	1580

Table 2. Total Pu concentrations in soil at different depths and sampling locations.

Soil Horizon	Depth	Pu-239 + 240	Pu-239 + 240
	cm	Bq/kg ± SD†	%
Pit 1			
A	0–16	3 920 ± 180	94.8
AB	16–27	140 ± 11	3.4
Bk1	27–58	18 ± 4.5	0.4
Bk2	58–76	5.6 ± 1.0	0.2
Bg	76–103	45 ± 5.0	1.0
2BCg	103–123	5.0 ± 0.5	0.1
Pit 2			
A	0–7	5 920 ± 770	58.4
Bw	7–19	4 120 ± 160	40.7
Bt	19–50	78 ± 4.7	0.8
2Bt	50–105	12 ± 2.7	0.09
3BCgk1	105 +	1.2 ± 0.3	0.01
Pit 3			
A	0–18	7 750 ± 345	97.1
AB	18–35	200 ± 15	2.5
Bw	35–51	8.3 ± 1.0	0.18
BC	51–120	18 ± 1.5	0.2
BCk1	120 +	1.7 ± 0.3	0.02
Pit 4			
A	0–18	6 630 ± 300	98.9
Bt1	18–41	42 ± 3.3	0.6
Bt2	41–77	22 ± 2.2	0.4
BCg	77–108	1.7 ± 0.7	0.01
2BCg	108 +	6.7 ± 0.7	0.09
Pit 5			
A	0–15	18 200 ± 1 030	92.5
Bt	15–48	1 470 ± 83	7.4
Btg	48–120	5.0 ± 1.0	0.1

† Standard deviation for all propagated uncertainties.